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New physical principles of contact thermoelectric cooling

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We suggest a new approach to the theory of the contact thermoelectric cooling (Peltier effect). The metal-metal, metal-n-type semiconductor, metal-p-type semiconductor, p-n junction contacts are analyzed. Both degenerate and non-degenerate electron and hole gases are considered. The role of recombination in the contact cooling effect is discussed by the first time.

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I. INTRODUCTION

It is well known [1] that the Peltier effect is the basis for solid thermoelectric cooling. The main point of it arises from the fact that the heat extraction or absorption occurs at the contact between two different conducting media if the d.c. electric current flows through this contact. Boundary conditions in an electric current contact have been discussed in a previous work. [2] Here we are interested in the heat flow. The absorption or extraction of heat (cooling or heating) depends on the current direction. The traditional approach to determine the quantity of this heat (Peltier heat) is based on the generalized thermal conductivity law, [3]

$$\mathbf{q} = -\kappa \nabla T + (\tilde{\mu} + \Pi)\mathbf{j} \tag{1}$$

where $\mathbf{q}$ is the heat flux density, κ is the thermal conductivity, T is the temperature, $\tilde{\mu} = \varphi + \mu/e_0$ is the electrochemical potential of the charge carriers, φ is the electric potential, μ is the chemical potential of the carriers, e_0 is the charge of the carriers, Π is the Peltier coefficient, $\mathbf{j}$ is the electric current density.

Let us suppose that the temperature gradient is absent in the electric circuit, and that the electric current flows through the contact of two media (Fig. 1). We assume also that the lateral sides of the circuit are adiabatically insulated, and that the circuit has a unit section.

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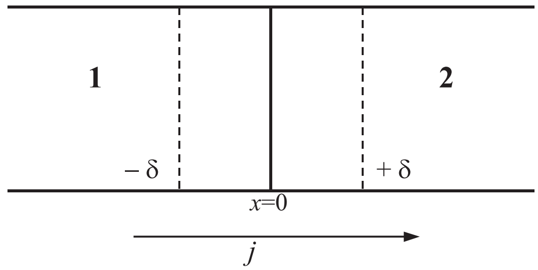

FIG. 1: Junction for the Peltier effect.

Let us choose the small volume bounded by the planes $x = \pm\delta$ near the contact $x = 0$, and calculate the Peltier heat Q_Π at this volume under the presence of the electric current (see Fig.1). In the linear approximation to the electric current (we neglect the Joule heating) this heat per unit time is equal to

$$Q_\Pi = -\int_V \nabla \cdot \mathbf{q}_\Pi dv = -\oint_S \mathbf{q}_\Pi \cdot d\mathbf{s}. \tag{2}$$

We integrate over the surface limiting the chosen volume in Fig.1. $\mathbf{q}_\Pi = \Pi\mathbf{j}$ is the Peltier heat density, $d\mathbf{s} = ds\mathbf{n}$, ds is the surface element, $\mathbf{n}$ is the external normal. For the simple chosen geometry it is straightforward to verify that in the limit $\delta \to 0$,

$$Q_\Pi = (\Pi_1 - \Pi_2)J, \tag{3}$$

where $\Pi_{1,2}$ are the Peltier coefficients of the first and the second materials, and J is the electric current. The quantity Q_Π determines the Peltier heat at the contact between the two media. Under fixed current direction $Q_\Pi > 0$ if $\Pi_1 > \Pi_2$ and the contact is heated. On the contrary, if $\Pi_1 < \Pi_2$, $Q_\Pi < 0$ and the contact is cooled. Actually the thermoelectric cooling modules are fabricated from two semiconductor brunches with electron (n) and hole (p) type conductivities.[1] Figure 2 illustrates the sketch of this module. Two semiconductors are coupled electrically in series and thermally in parallel. For non-degenerate electrons (n) and holes (p),[4]

$$\Pi_{n,p} = \mp\frac{1}{e}\left[(q_{n,p} + \frac{5}{2})T - \mu_{n,p}\right]. \tag{4}$$

Here T is the temperature in energy units, $\mu_{n,p}$ are the chemical potentials of electrons and holes which are measured from the bottom of the conduction band and the top of the valence band, respectively ($\mu_p = -\epsilon_g - \mu_n$, where ϵ_g is the band gap), e is the hole charge, $q_{n,p}$ are the exponents in the momentum relaxation times,[5]

$$\tau_{n,p}(\epsilon) = \tau^0_{n,p}\left(\frac{\epsilon}{T}\right)^{q_{n,p}}, \tag{5}$$

where ϵ is the energy of the carriers. The constant quantities $\tau^0_{n,p}$ and $q_{n,p}$ for different relaxation mechanisms can be found elsewhere.[5].

For degenerate electron and hole gases,

$$\Pi_{n,p} = \mp\frac{\pi^2}{3e}\left(q_{n,p} + \frac{3}{2}\right)\frac{T^2}{\mu_{n,p}}. \tag{6}$$

To understand the physical meaning of equations (4) and (6), it is convenient to rewrite these expressions as follows:

$$\Pi_{n,p} = \mp\frac{1}{e}\left[\langle\epsilon\rangle_{n,p} - \mu_{n,p}\right], \tag{7}$$

where $\langle\epsilon\rangle_{n,p}$ is the mean kinetic energy of the carriers in the flux,

$$\langle\epsilon\rangle_{n,p} = \frac{\int_0^\infty \tau_{n,p}(\epsilon)\epsilon^{5/2}\frac{df_0^{n,p}(\epsilon)}{d\epsilon}d\epsilon}{\int_0^\infty \tau_{n,p}(\epsilon)\epsilon^{3/2}\frac{df_0^{n,p}(\epsilon)}{d\epsilon}d\epsilon}. \tag{8}$$

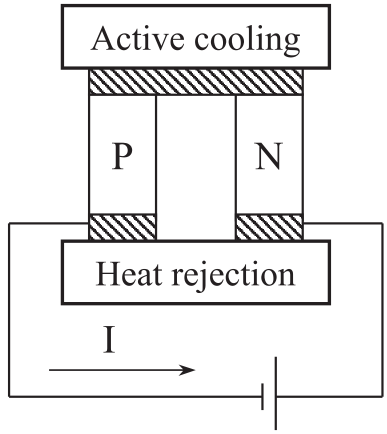

FIG. 2: Sketch of a thermoelectric cooling module.

where $f_0^{n,p}(\epsilon)$ are the Fermi-Dirac distribution functions. Notice that, similar to the chemical potentials, the mean energies $\langle\epsilon\rangle_{n,p}$ are measured from the bottom of the conduction band and the top of the valence band respectively. Often the chemical potentials $\mu_{n,p}$ are interpreted as the potential energies of electrons and holes.[4]

For non-degenerate statistics ($|\mu| \gg T, \mu < 0$),

$$\langle\epsilon\rangle = \left(q + \frac{5}{2}\right) T, \tag{9}$$

while for the degenerate case ($|\mu| \gg T, \mu > 0$),

$$\langle\epsilon\rangle = \mu + \frac{\pi^2 T^2}{3\mu}\left(q + \frac{3}{2}\right). \tag{10}$$

To demonstrate the physical meaning of the Peltier effect, a metal-n-type semiconductor contact is usually used (see Fig.3). It is easy to see that the surplus of the electron energy in the semiconductor, in comparison with the metal, is $\Delta\epsilon = \langle\epsilon\rangle - \mu_n = (q + 5/2)T - \mu_n$, and $\Pi_1 - \Pi_2 = \Delta\epsilon/e$.

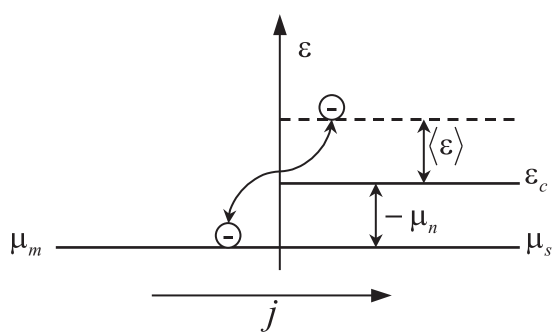

FIG. 3: Heating of metal-n-type semiconductor contact.

The obtained result is clear for this type of contact. At the same time these contacts are not really used in applications. The consideration of other contacts do not have the same obvious understanding, and a priori the following questions arise:

- What does the potential energy for the degenerate gas of the charge carriers mean?
- What is the physical meaning of the energy change in a metal-p-semiconductor contact and in a p-n junction?
- Why does the approach stated above ignore the work of the built-in electric field within the contact?

- It is easy to show that the value $\langle\epsilon\rangle - \mu$ in any type of contacts is different on the left and on the right from the contact plane. Therefore, the description of the contact refrigeration based on the consideration of the separate electron transitions is not valid. One needs to take into account the statistics of these transitions. How to reflect this fact in the preceding scheme?

II. MECHANISMS OF CONTACT THERMOELECTRIC COOLING

In the usual scheme of n-n or p-p junctions the contact heating or cooling is explained by the electron (hole) transitions between $\langle\epsilon\rangle$ - levels (see Fig.4). The latter are counted from the common Fermi level. In p-n junctions it is necessary to take into account the electron-hole generation and recombination. These are the processes that determine contact cooling and heating. In most works devoted to discuss this problem, the recombination rate is assumed to be infinite.

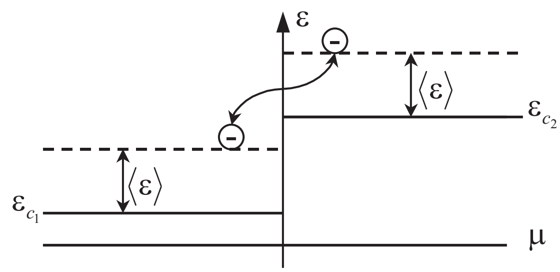

FIG. 4: Contact in equilibrium ($j = 0$)

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Here we present some new assumptions. Let us consider first the n-n contact between non-degenerate semiconductors (Fig.5). If the momentum scattering in both semiconductors is the same, then [see Eq.(7)],

$$\begin{aligned} \Pi_1 - \Pi_2 &= \frac{(\mu_1 - \mu_2)}{e} \\ &= \frac{(\chi_1^0 - \chi_1 - \chi_2^0 + \chi_2)}{e} = \varphi_c + \frac{\Delta\epsilon_c}{e}, \end{aligned} \tag{11}$$

where $\varphi_c = (\chi_2 - \chi_1)/e$ is the contact voltage, and $\Delta\epsilon_c = \chi_1^0 - \chi_2^0$ is the work of a valence force. This means that the contact cooling or heating is connected with the work of the built-in electric field W_c and the work of the valence forces W_ν. The total work is $W = Q_\Pi = W_c + W_\nu$, where $W_c = J\varphi_c$ and $W_\nu = J\Delta\epsilon_c/e$. Here the valence force is caused by the abrupt change of the conduction band. A similar reasoning is valid for the p-p junction.

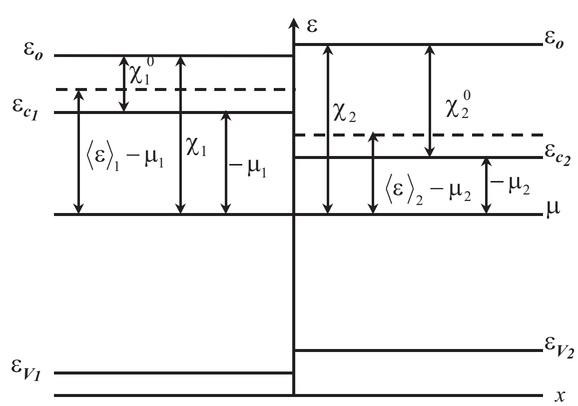

FIG. 5: Contact of non-degnerate semiconductors. ϵ_0 is the vacuum level; χ_i and χ_{i^0} are workfunctions and electron affinities, respectively.

If we have the $n^+ - n$ or $p^+ - p$ junction, the Peltier effect does not depend on the contact properties, and it is determined only by the parameters of the non-degenerate semiconductor (see Fig.3),

$$\Pi_1 - \Pi_2 = -\frac{\mu_n}{e}. \tag{12}$$

In the case of a contact between two degenerate n- or p-type semiconductors (or two metals) the Peltier effect depends on the contact properties again (see Figs.6 and Eq.(10)), and the work of the built-in electric field jointly with the work of the valence forces occurs. Now

$$\Pi_1 - \Pi_2 = \frac{\pi^2}{3e}\left(q + \frac{3}{2}\right)\frac{T^2}{\mu_1\mu_2}(\mu_1 - \mu_2). \tag{13}$$

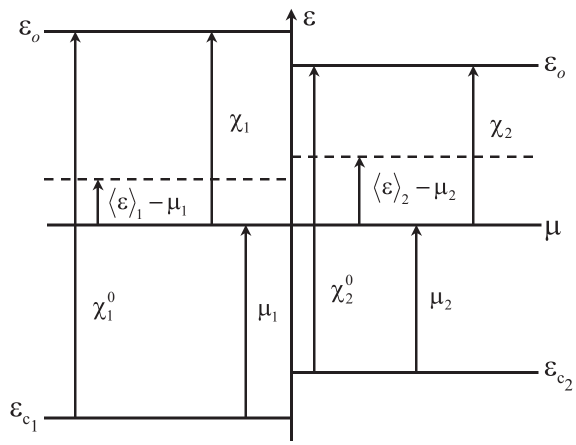

FIG. 6: A contact between two metals.

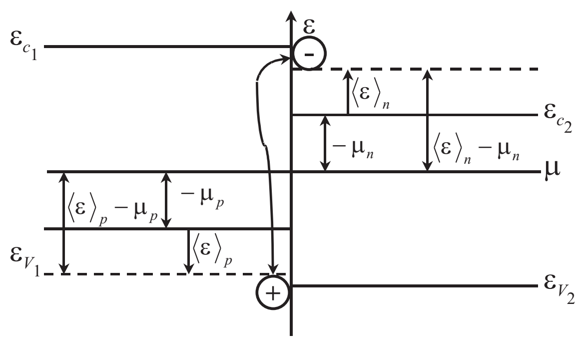

FIG. 7: A p-n junction.

Comparing (10) and (12) we see that the Peltier heat in the contact between degenerate materials is essentially less than that in the contact between the non-degenerate semiconductors.

Let us note also that the work of the built-in electric field and the valence forces give rise to the qualitatively different temperature of the contacts in the case of non-degenerate and degenerate brunches of the circuit. In the former

$$W_c \propto \frac{3}{2}(T(E) - T_0). \tag{14}$$

where $T(E)$ is the non-equilibrium temperature, E is the built-in electric field, T_0 is the room temperature. In the latter,

$$W_c \propto \frac{\pi^2}{4}\frac{T^2(E) - T_0^2}{\mu}. \tag{15}$$

Let us examine the p-n junction (Fig.7). It is easy to see from Fig.7 that

$$\Pi_1 - \Pi_2 = -\frac{\mu_n + \mu_p}{e}. \tag{16}$$

The generation or recombination at the contact causes the Peltier heating or cooling in this case. In addition, Eq.(15) corresponds to the infinitely strong recombination rate. At the same time there are a lot of situations when this rate is weak enough. What has happened with the Peltier effect in this case? The situation is similar to the electric current or thermoelectric current in the bipolar semiconductors. [6, 7] The Fermi quasilevels must appear causing the redistribution of carriers concentrations, electric fields and conductivity. As a result the nature of the Peltier effect can drastically change. It follows from Fig.8 that under the chosen current direction the cooling exchanges to the heating if the recombination is absent. We do not present here the detailed calculations, and give only the main equations for this problem.

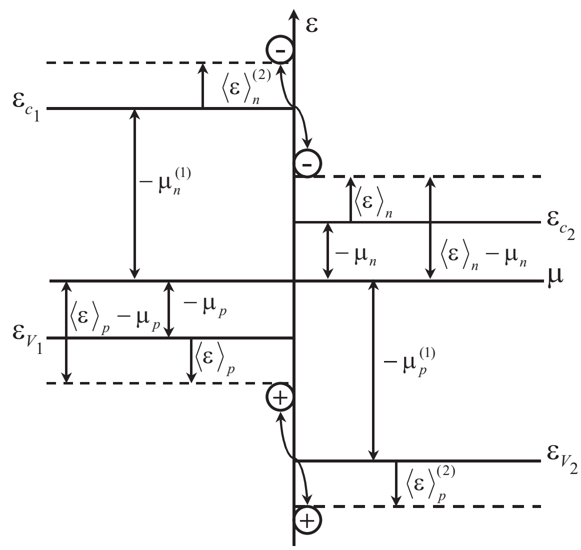

FIG. 8: *A p-n junction without recombination.*

III. MAIN EQUATIONS

The general approach to the problem of the contact cooling or heating accounting for the generation and recombination processes requires the solution of the following set of equations:

$$\begin{gathered}\nabla \cdot \mathbf{j}_n = eR_n, \nabla \cdot \mathbf{j}_p = -eR_p, \\ \nabla\varphi(x) = 4\pi e(\delta n - \delta p).\end{gathered} \tag{17}$$

Here $\mathbf{j_{n,p}}$ are the electron and hole electric current densities; δn, δp are the concentrations of non-equilibrium electrons and holes, and $R_{n,p}$ are the electron and hole recombination rates.
A rigorous theory of recombination suggests that R_n is identically equal to R_p and therefore for all recombinatiion mechanisms in a linear approximation we have [2, 8]

$$R_n = R_p = R = \frac{\delta n}{\tau_n} + \frac{\delta p}{\tau_p}. \tag{18}$$

The values of $\tau_{n,p}$ are material parameters having the dimension of time, but they are not electron and hole lifetimes. However, when the condition of quasi-neutrality holds [9] ($r_d \ll a^2$, where r_d is the Debye radius and a is the width of the p-n junction), as it is often the case, the non-equilibrium electron and hole concentrations are equal ($\delta n = \delta p$). In this case one can define a lifetime common to electrons and holes as

$$\frac{1}{\tau} = \frac{1}{\tau_n} + \frac{1}{\tau_p}. \tag{19}$$

From a previous work,[8] it follows that $\tau_n/\tau_p = n_0/p_0$; therefore, the lifetime of non-equilibrium carriers can be expressed as

$$\tau = \tau_n \frac{p_o}{n_0 + p_0}. \tag{20}$$

As it is well known, [9] using Poisson equation in a quasi-neutrality approximation becomes unnecessary, and the electric potential at the boundary of two semiconductors displays jump-like changes. The boundary conditions to Eqs.(16)-(18) can be found elsewhere. [2] The surface recombination rates present in these boundary conditions are [8, 10]

$$R_s = S_n \delta n + S_p \delta p, \tag{21}$$

where S_n and S_p are the parameters characterizing the contact properties. If the quasi-neutrality conditions ($\delta n = \delta p$) are satisfied, a surface recombination rate common to electrons and holes can be introduced:

$$S = S_n + S_p. \tag{22}$$

Therefore one can write

$$R_s = S\delta n. \tag{23}$$

IV. FURTHER DISCUSSION AND CONCLUSIONS

In this section we will present qualitative arguments regarding the two limiting cases of very strong and very weak recombination rates. The criteria for these rates have been discussed in [6]. According to those results, the surface and the bulk recombination rates are strong if $S \gg S_0$, or $\tau_n \ll \tau_0$ respectively, where $S_0 = (n_0 + p_0)\sigma_p^2 T_0/(\sigma_n + \sigma_p)e^2 a n_0 p_0$, n_0 and p_0 are the equilibrium concentration of electrons and holes, σ_n and σ_p and are the electron and hole conductivity; $\tau_0 = e^2 a n_0 T_0(\sigma_n + \sigma_p)/(\sigma_n \sigma_p)$. The inequalities $S \ll S_0$ and $\tau_n \gg \tau_0$ determine the weak surface and bulk recombination. If the strong recombination occurs, then the physical process in the p-n junction is as in Fig.7, and Eq. (12) is right. In the opposite case (weak recombination), electrons from the n-region will pass to the p-region and occupy the states with mean energy $\langle\epsilon\rangle_n$ (cf. Fig.8). By analogy holes will pass to the n-region and will occupy the states with the mean energy $\langle\epsilon\rangle_p$. In the latter case, under the appropriate current direction, the contact is heated and the cooling is absent.

In conclusion, we wish to emphasize that the contact refrigeration is a promising field for applications in different spheres of human activity. In particular, a proper description of the physical processes involved is very important in the today's problem of acheaving high values of the figure of merit Z for thermoelectric materials. [11] All the efforts devoted to this problem up to now [12] have been based on the expression $Z = (\alpha_n + \alpha_p)^2/(\sqrt{\kappa_n \rho_n} + \sqrt{\kappa_p \rho_p})^2$ [1]or in the simpler expression $Z = \alpha^2\sigma/\kappa$. Here $\alpha_{n,p}$, $\kappa_{n,p}$ and $\rho_{n,p}$ are, respectively, electron and hole thermoelectric power, thermal conductivity and electric resistance. α and σ are the thermoelectric power and the electric conductivity of an effective medium.

We want to underline that in thermoelectricity this expression is good for the circuit consisting of the metal and semiconductor of n-type and for another materials if the surface and the bulk recombination is very strong. At the same time this formula must be revised in the case of the contacts metal-p-semiconductor and in p-n junctions, where the recombination processes are essential even in the linear approximation. [6, 7] Especially important is to take into account the recombination processes in p-n junctions in thin-film thermoelectric cooling modules (Fig.2).

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